The Variational Calculation of Bulk Moduli for Liquid Binary Alloys of Alkali Metals

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The bulk moduli of the Na–K, Na–Cs, and K–Rb liquid equiatomic alloys at $T = 373$ K are calculated by the variational method with the hard-sphere reference system. The local Animalu–Heine model pseudopotential and Toigo–Woodruff exchange-correlation function are used for the calculation. A good agreement with experimental data is achieved.

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1. Introduction

The variational [1] method with the additive hard-sphere (HS) reference system had been applied to investigation of binary liquid metal alloys for the first time in the work [2]. Since then, it continues to be used in this field (for example, [3–10]; see also the review [11]). In our previous studies of liquid alkali-metal's alloys [12–15] by different methods of the thermodynamic perturbation theory (TPT) including the variational one, it was shown that the Animalu–Heine (AH) model pseudopotential (MP) [16] in the local approximation [17] allows to obtain very good results for such thermodynamic characteristics as the Helmholtz free energy, internal energy, entropy, and their mixing quantities. In the present work, the applicability of the named pseudopotential for calculating the bulk moduli of liquid alkali-alkali metal alloys is estimated on the example of Na–K, Na–Cs, and K–Rb equiatomic alloys near their melting temperatures in the framework of the HS variational method.

2. Theory

One of the ways to define the bulk modulus, B_T, is the following (hereafter, per atom):

$$B_T = \Omega \left(\partial^2 F/\partial \Omega^2\right)_T , \tag{1}$$

where Ω is the mean atomic volume, F is the Helmholtz free energy, T is the temperature. Here, we solve Eq. (1) numerically using F found by the variational method.

In the first-order of the high temperature approximation (HTA) of the TPT [18] the Helmholtz free energy is (hereafter, the quantities characterizing the reference system and perturbation are labelled with the subscripts "0" and "1", respectively)

$$F_{\rm HTA} = F_0 + \langle U_1 \rangle_0 , \tag{2}$$

where U is the potential energy;

$$\langle U_1 \rangle_0 = \frac{2\pi}{\Omega} \int_0^\infty \phi_1(r) g_0(r) r^2 \, {\rm d}r. \tag{3}$$

Here, $\phi(r)$ is the pair interatomic potential and $g(r)$ is the pair correlation function.

As a rule, to construct an effective pair potential for a simple metal the nearly-free-electron (NFE) approximation is used (hereafter, in atomic units (a.u.)):

$$\phi_{\rm NFE}(r) = \frac{z^2}{r} + \frac{\Omega}{8\pi^2} \int_0^\infty F(q) \frac{\sin(qr)}{qr} q^2 \, {\rm d}q, \tag{4}$$

where z is the valence and $F(q)$ is the energy wave-number characteristic.

Within the HS variational method Eqs. (2),(3) are transformed to the following:

$$F_{\rm var-HS} = F_{\rm HS} + \frac{2\pi}{\Omega} \int_\sigma^\infty \phi(r) g_{\rm HS}(r) r^2 \, {\rm d}r, \tag{5}$$

where σ is the HS diameter.

For the binary simple-metal mixture Eq. (5) is rewritten as follows:

$$F^{\rm bin}_{\rm var-HS-NFE} = F^{\rm bin}_{\rm HS} + U^{\rm bin}_e - T S^{\rm bin}_e + \frac{2\pi}{\Omega^{\rm bin}} \sum_{i,j=1}^{2} c_i c_j \int_{\sigma_{ij}}^\infty \phi_{{\rm NFE}ij}(r) g_{{\rm HS}ij}(r) r^2 \, {\rm d}r, \tag{6}$$

where U_e is the electron contribution to the internal energy calculated here using the Nozieres–Pines approximation for the exchange-correlation energy [19], S_e is the electron contribution to the entropy, c_i is the concentration of the i-th component; $\phi_{ij}(r)$, $g_{ij}(r)$ and σ_{ij} are the partial characteristics: pair potential, pair correlation function and HS diameter, respectively. To calculate $F^{\rm bin}_{\rm HS}$ the analytical expression obtained by Umar et al. [20] is used. Since the calculating procedure is carried out in the wave space, the HS partial structure factors, $S_{{\rm HS}ij}(q)$, instead of $g_{{\rm HS}ij}(r)$, are needed for the calculation. We use the analytical expressions of $S_{{\rm HS}ij}(q)$ in the Ashcroft–Langreth form [21].

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The generalization of Eq. (4) to the binary alloy is trivial:

$$\phi_{\mathrm{NFE}ij}(r) = \frac{z_i z_j}{r} + \frac{\Omega^{\mathrm{bin}}}{8\pi^2}\int_0^\infty F_{ij}(q)\frac{\sin(qr)}{qr}q^2\,\mathrm{d}q, \quad (7)$$

where

$$F_{ij}(q) = -\frac{\Omega^{\mathrm{bin}}q^2\omega_i(q)\omega_j(q)}{8\pi} \times \left[(\varepsilon_{\mathrm{H}}^{\mathrm{bin}}(q)-1)^{-1} + (1-f^{\mathrm{bin}}(q))\right]^{-1}. \quad (8)$$

Here, z_i is the valence of the i-th component, $\varepsilon_{\mathrm{H}}(q)$ is the Hartree dielectric function, $f(q)$ is the exchange-correlation function, which is taken here in the Toigo–Woodruff form [22]; $\omega_i(q)$ is the pseudopotential form-factor of the unscreened i-th kind ion, which for the local AH (LAH) model is expressed as follows:

$$\omega_{\mathrm{LAH}i}(q) = \frac{4\pi}{\Omega^{\mathrm{bin}}q^2} \times \left[(A_i R_{\mathrm{M}i} - \bar{z})\cos(qR_{\mathrm{M}i}) - \frac{A_i R_{\mathrm{M}i}\sin(qR_{\mathrm{M}i})}{qR_{\mathrm{M}i}}\right] \times \exp\left(-0.03\left(\frac{q}{2k_{\mathrm{F}}^{\mathrm{bin}}}\right)^4\right), \quad (9)$$

where $\bar{z} = c_1 z_1 + c_2 z_2$ is the mean alloy valence, A_i and $R_{\mathrm{M}i}$ are the i-th component parameters taken the same as ones for the corresponding pure metals from [17] (Table I); $k_{\mathrm{F}} = \left(3z\pi^2/\Omega\right)^{1/3}$ is the Fermi wave vector.

TABLE I

Values of the pseudopotential parameters used for calculations (in a.u.)

Parameter	Na	K	Rb	Cs
$R_{\mathrm{M}i}$	2.1148	2.9990	3.3641	3.8677
A_i	–0.1958	–0.1853	–0.1874	–0.1838

The minimization of $F^{\mathrm{bin}}_{\mathrm{var-HS-NFE}}$ is performed with respect to σ_{11}, σ_{22} and Ω^{bin}. The last minimization corresponds to the condition that the pressure is equal to zero.

3. Results and discussion

The results obtained for Na–K, Na–Cs, and K–Rb equiatomic alloys at $T = 373$ K are summarized in Table II in comparison with experimental data [23, 24] and other theoretical results obtained by the HS variational method [3–5] and by methods of the dynamic theory of liquids [25, 26].

The following pseudopotentials are used in aforementioned theoretical works: the Harrison first-principles pseudopotential [27] extended to binary alloys [28, 29] in [3]; the non-local MP of Wang et al. [30] with higher-order terms of the pseudopotential perturbation theory in [4]; the local MP of Heine and Abarenkov [31] in [5]; the local MP of Ashcroft [32] in [25] and the first-principles pseudopotential of Troullier and Martin [33] in [26].

TABLE II

Bulk modulus, B_T [10^{10} dyne/cm^2], at $T = 373$ K

Equat. alloy	Calculation						Exp.
	Hafner [3]	Lai [4]	Yilmaz [5]	Jain [25]	Thakur [26]	This work	
Na-K	2.6	3.45	5.07	3.65	3.87	3.2	3.3 [23]
Na-Cs	1.7	2.56	5.21	–	–	2.5	2.0 [24]
K-Rb	1.4	–	–	–	–	2.0	2.2 [24]

The difference between our result and experiment is 3% for Na–K, 10% for K–Rb and 20% for Na–Cs. It is correlated well with our previous works on other thermodynamic properties [11, 13] where an agreement with experimental data for Na–K, K–Rb and Na–Rb alloys was better than for alloys of alkali metals containing Cs. All our results are more satisfactory in comparison with experiment than results of other theoretical works except for Hafner's result for Na–Cs (Table II).

4. Conclusion

The work fulfilled shows the usefulness of the Animalu–Heine model pseudopotential in the local approximation for an accurate description of such an elastic deformation property as the bulk modulus for binary liquid alloys of alkali metals in the framework of the variational approach.

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